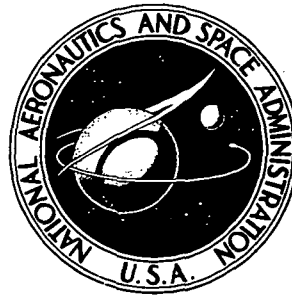


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INFLUENCE OF VARIOUS SURFACE
PRETREATMENTS ON ADHERENCE OF
SPUTTERED MOLYBDENUM DISULFIDE
TO SILVER, GOLD, COPPER, AND BRONZE

by Talivaldis Spalvins

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Cleveland, Ohio 44135

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16. Abstract Solid-film lubricants of radio-frequency sputtered molybdenum disulfide (MoS_2) were applied to silver, gold, copper, and bronze surfaces that had various pretreatments (mechanical polishing, sputter etching, oxidation, and sulfurization). Optical and electron transmission micrographs and electron diffraction patterns were used to interpret the film-formation characteristics and to evaluate the sputtering conditions in regard to the film and substrate compatibility. Sputtered MoS_2 films flaked and peeled on silver, copper, and bronze surfaces except when the surfaces had been specially oxidized. The flaking and peeling is a result of sulfide compound formation and the corresponding grain growth of the sulfide film. Sputtered MoS_2 films showed no peeling and flaking on gold surfaces regardless of surface pretreatment.			
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INFLUENCE OF VARIOUS SURFACE PRETREATMENTS ON ADHERENCE OF SPUTTERED MOLYBDENUM DISULFIDE TO SILVER, GOLD, COPPER, AND BRONZE

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SUMMARY

Molybdenum disulfide (MoS_2) films were radio-frequency sputtered onto silver, gold, copper, and bronze surfaces. These surfaces had four different pretreatments before the MoS_2 film was deposited (mechanical polishing, sputter etching, oxidation, and sulfurization). Optical and electron transmission micrographs and electron diffraction patterns were taken to interpret the film-formation characteristics and to evaluate the sputtering conditions in regard to film and substrate compatibility. These micrographs revealed that sputtered MoS_2 films flaked and peeled on mechanically polished, sputter etched, or sulfurized silver, copper, and bronze surfaces. Copper and bronze surfaces which were specially oxidized exhibited strong adherences. Sputtered MoS_2 films on gold surfaces, regardless of the surface pretreatment, had strong adherence. The flaking and peeling of the film is a result of sulfide compound formation between the sputtered MoS_2 film and the substrate as observed from the reaction zones of the micrographs.

INTRODUCTION

When sputtered molybdenum disulfide (MoS_2) films are applied to surfaces for lubrication, only extremely thin films of the order of 200 nanometers (2000 \AA) thick, minimum, are required. Sputtered MoS_2 films show great promise and are gaining increased recognition for industrial applications. Thin sputtered films are of great interest, especially where a lubricant is needed and the clearances are very critical such as in ball-bearing applications. Molybdenum disulfide films deposited by sputtering generally exhibit exceptionally long wear lives and maintain a low coefficient of friction in vacuum, dry air, or in inert-gas atmospheres (ref. 1).

The unique features of the sputtering process include the surface pretreatment (sputter etching), which changes the surface chemistry and topography, and the relatively high kinetic energy of the sputtered material (ranging up to 20 eV) with which it strikes the substrate. As a result, the film material penetrates the substrate several lattice parameters and forms an interface which contributes to the good adherence of the film to the substrate. The long wear life of these sputtered films has been attributed to their strong adherence to the substrate.

Since the application of sputtered materials as solid-film lubricants on ball bearings, sliding surfaces, or rotating surfaces is a relatively recent development, only a limited number of substrate materials have been coated with sputtered MoS₂. The sputtered MoS₂ films thus far have been deposited on materials such as stainless steels, tool steels, nickel, Inconel, aluminum, cobalt, and glass. In these instances, there was strong adherence of the film to the substrate, as determined by friction and tensile tests (ref. 1). It has been observed, however, that sputtered MoS₂ films, when deposited on bronze ball-bearing components, exhibit inferior lubrication properties. This is believed to be a consequence of poor adherence between the film and the substrate. It is important to recognize the factors which contribute to poor adherence during sputtering. The substrate temperature during MoS₂ sputtering determines the degree of film adherence and the friction characteristics (ref. 2).

In this investigation, MoS₂ was sputtered onto silver, gold, copper, and bronze surfaces. The surfaces of these noble metals were either mechanically polished, sputter etched, oxidized, or sulfurized before the MoS₂ film was sputtered on. The objectives of this study were to analyze by optical and electron transmission microscopy and electron diffraction the film-formation characteristics on the surfaces with the different pretreatments and to evaluate the adherence in terms of the compatibility of the materials.

APPARATUS

The apparatus used for sputtering the MoS₂ films was a radio-frequency-diode system with superimposed dc bias, as shown schematically in figure 1. The apparatus is described in reference 1. The sputtering parameters used in this investigation were the same as those used in previous studies and were as follows: frequency, 7 megahertz; argon pressure, approximately 2.4 newtons per square meter ($\approx 1.8 \times 10^{-2}$ torr); radio-frequency power input, 420 watts; reflected power, approximately 1 watt; input, 500 volts dc; target voltage, 1.25 to 1.35 kilovolts ac; distance between target and specimen, approximately 2.5 centimeters.

SPECIMEN PREPARATION

The mechanically polished surfaces were ground with 400- and 600-grade emery papers. They were then finished with levigated alumina on a lapping wheel and then transferred to the sputtering apparatus for MoS_2 deposition.

The dc-sputter-etched surfaces before etching were mechanically polished as described and were then cleaned by sputter etching. During sputter etching, the surface is cleaned of oxide layers and skin effects of cold working that are produced with mechanical polishing. Sputter etching also changes the surface topography by exposing grain boundaries and various planes. This change has a microscopic "roughening" effect on the surface. The purpose of sputter etching is to clean the surface prior to deposition, so that the sputtered MoS_2 film is applied directly to a clean surface.

The copper surfaces that were specially oxidized were placed in a high-temperature furnace at atmospheric conditions and heated to 425°C . During the heating process, the thickness of the oxide film that was formed was observed by the interference color changes that accompany the film growth, as tabulated by Kubaschewski and Hopkins (ref. 3). An oxide film 120 to 160 nanometers (1200 to 1600 \AA) thick was formed before the surface was covered with a sputtered MoS_2 film.

Sulfurization of the specimen surfaces was performed by heating them in hydrogen sulfide (H_2S) gas for 5 minutes.

The above surface pretreatments were performed on polycrystalline silver, gold, copper, and bronze specimens. In one instance, MoS_2 was sputtered directly on mechanically polished single crystals of silver, gold, and copper.

RESULTS AND DISCUSSION

Characterization of Sputtered MoS_2 Films by Optical Microscopy

In one instance during the sputtering experiments, MoS_2 was sputtered onto one set of highly polished, single crystal surfaces of silver, gold, and copper. The films on these surfaces are shown in figure 2. Film flaking and peeling occurred on the copper and silver surfaces, but there was strong adherence between the gold and the sputtered MoS_2 film.

In the following discussion, all substrate materials used were polycrystalline. To evaluate the surface effects on the film adherence, polycrystalline copper and silver disks were mechanically polished and then transferred to the sputtering chamber for film deposition. Another series of specimens were also mechanically polished, but before film deposition, the surfaces were sputter etched to clean off the contaminants

and oxides. Both the mechanically polished and sputter-etched surfaces revealed poor adherence when sputtered with MoS_2 . This implies that the surface condition during deposition of MoS_2 had no effect on the film adherence. In a number of instances, even during the sputtering process, flaking and scaling of MoS_2 occurred on the copper surface. Typical micrographs of the film appearance on copper surfaces are shown in figures 3 to 5.

Observation of the sputtered MoS_2 film showed film reaction with the substrate and consequent blistering (fig. 3). Observation of a randomly selected, isolated area on the copper surface revealed the formation of sulfur reaction islands and the eventual lifting of the film from the surface (fig. 4). Finally, the joining of isolated reaction islands and complete film lifting were observed (fig. 5). Similar effects were also observed with bronze surfaces sputtered with MoS_2 .

For comparison purposes, figure 6 shows the microstructure of a film of MoS_2 sputtered, during the same experiment, on a glass slide that was coated on one half with a copper film. The area where MoS_2 was directly sputtered onto the glass showed a continuous, smooth, strongly adherent film. The area where MoS_2 was deposited on the copper film, however, showed definite reaction zones with blistering (fig. 6). Similar effects and appearances were also observed with silver surfaces, as shown in figures 7 and 8. A 440C steel disk was first ion plated with a silver film and subsequently was sputtered with MoS_2 . Microscopic examination distinctly showed the areas where the MoS_2 film had flaked or lifted off the surface.

Characterization of Sputtered MoS_2 Films by Transmission

Electron Microscopy and Electron Diffraction

Electron transmission microscopy and electron diffraction were performed on 30- to 50-nanometer- (300- to 500-Å-) thick, sputtered MoS_2 films on thin copper foils. The MoS_2 films were stripped from the copper by dissolving the substrate in a dilute nitric acid solution. The etchant was selected on the basis that it is inert to MoS_2 . Electron diffraction micrographs confirmed the identity of MoS_2 and revealed that the film had a crystallite size between 10 and 20 nanometers (100 and 200 Å). A typical electron diffraction pattern is shown in figure 9, and the corresponding transmission micrographs are shown at magnifications of 85 000 and 10 000 in figure 10. The large, white areas in the micrographs are voids where particles or grains of possibly copper-sulfur or copper-molybdenum-sulfur reaction compounds were leached out during the dissolution of the copper substrate. At the lower magnification of 10 000, the leached-out grains can be distinctly identified. Molybdenum disulfide films applied on nickel and

mica substrates under sputtering conditions identical to those of this study and examined in the same manner were found to have, on the basis of electron diffraction patterns (ref. 1), an amorphous-like structure.

On copper, the crystallite size became apparent, as shown by the electron diffraction and transmission micrographs. These micrographs indicate the poor adherence which is a result of the grain growth and the possible formation of copper sulfide compounds.

Sputtering Effects on MoS₂ Film Formation

The method of MoS₂ application is one of the determining factors whether a sulfide is formed, since the energy provided by the deposition method tends to initiate a chemical as well as a physical reaction. When the MoS₂ lubrication mechanisms are discussed in the literature, the reaction between MoS₂ and the substrate has often been suggested (ref. 4). It has been proposed that, under some conditions, the MoS₂ and the metal surface will react and form a metal sulfide. The activation energy may be negligible when the conventional application methods are used. Nevertheless, the formation of substrate metal sulfide has been reported. When MoS₂ is applied by sputtering, the atoms that are knocked off the MoS₂ target by the high-velocity argon ions possess relatively high kinetic energies (up to 20 eV). The energetic sputtered atoms strike the specimen surface with a high velocity and thus have sufficient energy to promote reaction with the substrate and even penetrate a few lattice parameters.

It should be remembered that during sputtering of any material, the film is formed by the dislodged atoms and molecules. During sputtering of MoS₂, it is believed that free sulfur is liberated and excited to a highly energetic state and therefore is very prone to react chemically with the surface. It should be noted that during radio-frequency sputtering, three basic effects occur at the surface: (1) the sputtered material strikes the surface in an excited state, (2) many other energetic species (e.g., electrons and ions) affect the surface and the film-formation characteristics, and (3) the specimen is heated to an extent that depends on the power input into the target. All these influential factors act at the same time during the sputtering process and thus affect the film-formation characteristics.

The strong adherence of sputtered films is generally attributed to the sputter-etched surface and the energetics of the sputtered material. It is interesting to note, however, that when MoS₂ is sputtered on copper and silver surfaces, these two factors are detrimental to surface adherence. The factor which is of paramount importance during sputtering is the compatibility of the film and substrate. During MoS₂ sputtering, the free energetic sulfur atoms that may be liberated would tend to react chemically

with copper and silver. The formation of this sulfide reaction product is believed to be responsible for the poor adherence. The possibility of copper sulfide and silver sulfide formation under equilibrium conditions at temperatures above 100⁰ C is shown by the copper-sulfur and silver-sulfur phase diagrams (figs. 11 and 12). The gold-sulfur phase diagram has not been determined, since no chemical reactions have been observed. In this investigation, the reaction is induced by the sputtering process, which is a plasma, or high-energy, deposition method. The copper-sulfur and silver-sulfur phase diagrams additionally substantiate the chemical reaction and sulfide formations. It should be noted that examination of sputtered MoS₂ films on gold by electron transmission microscopy did not reveal grain growth or void formation; this indicates that gold has no tendency to form sulfides.

Sputtered MoS₂ on Oxidized and Sulfurized Surfaces

Copper and bronze surfaces were specially oxidized at elevated temperatures in a high-temperature furnace to form an oxide layer about 120 to 150 nanometers (1200 to 1500 Å) thick. Figure 13 shows the appearance of MoS₂ film on four specimens (a polished disk and an oxidized disk of copper, and a polished disk and an oxidized disk of bronze). All four specimens were sputtered with MoS₂ during the same experiment. Figure 13 indicates that the oxidized surfaces showed no flaking or peeling of the film. It is believed that the oxide film was thick enough to function as a barrier to prevent sulfide formation on the copper surface. The polished copper surface showed poor adherence (this has already been illustrated earlier in this report).

In another experiment, silver, gold, and copper were heated in H₂S gas for 5 minutes and subsequently were sputter coated with a MoS₂ film. The sulfurized silver and copper surfaces with sputtered MoS₂ films showed very poor adherence, but the gold surface, as expected, showed no flaking or peeling. Figure 14 shows the sulfurized and polished silver disks and the sulfurized gold disk. Flaking of the film is seen on both silver disks, regardless of the surface condition. The gold surface, exposed to H₂S, showed strong adherence, because of its inertness to sulfur.

SUMMARY OF RESULTS

When molybdenum disulfide (MoS₂) films are deposited for lubrication on various substrate materials, it is important not only to consider and evaluate the unique sputtering parameters, but also to consider the compatibility of the materials, especially in terms of possible chemical reactions and formation of surface compounds. Molybdenum

disulfide was sputtered on copper, silver, gold, and bronze with different surface pre-treatments, and the following results were observed:

1. Sputtered MoS_2 had poor adherence on silver, bronze, and copper surfaces that had been mechanically polished, sputter etched, or sulfurized. The poor adherence is believed to be due to the sulfide formation.
2. Sputtered MoS_2 had strong adherence on preoxidized copper and bronze surfaces.
3. Sputtered MoS_2 showed no flaking on gold surfaces that had been polished, sputter etched, or sulfurized. The good adherence is believed to be due to surface inertness for sulfide formation.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 7, 1972,
502-01.

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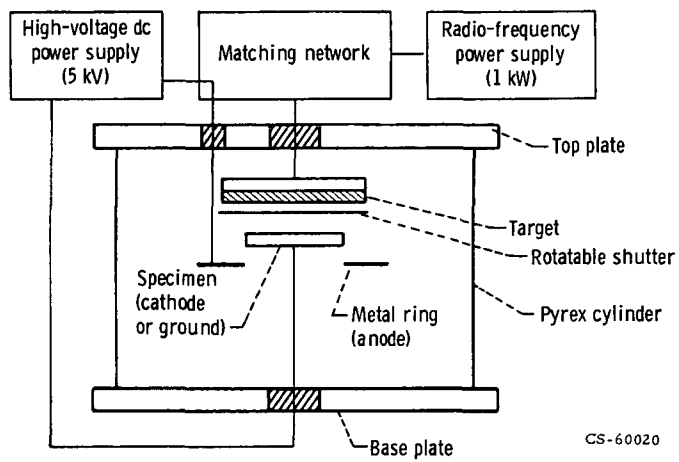
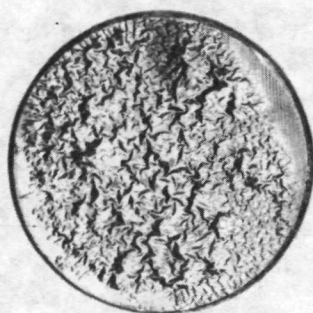
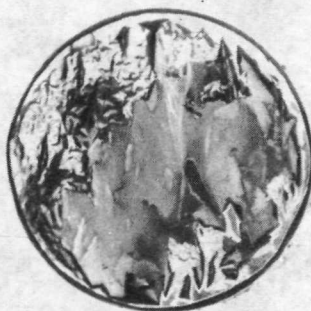
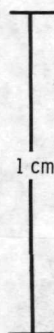


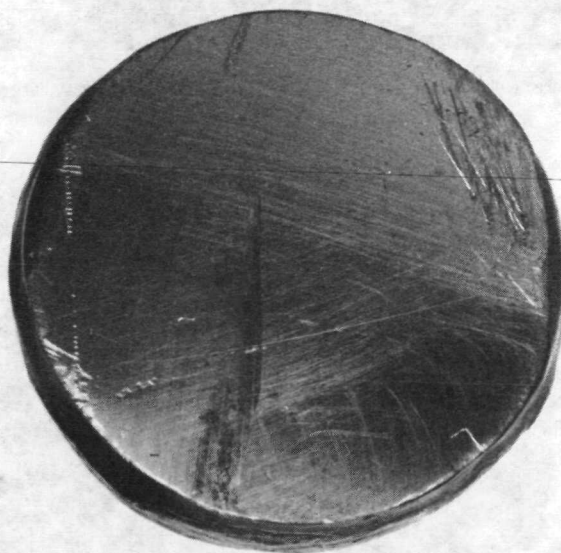
Figure 1. - Radio-frequency sputtering system with dc bias.



Flaked film on silver



Flaked film on copper



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Adherent film on gold

Figure 2. - Sputtered molybdenum disulfide film on single crystals of silver, copper, and gold.

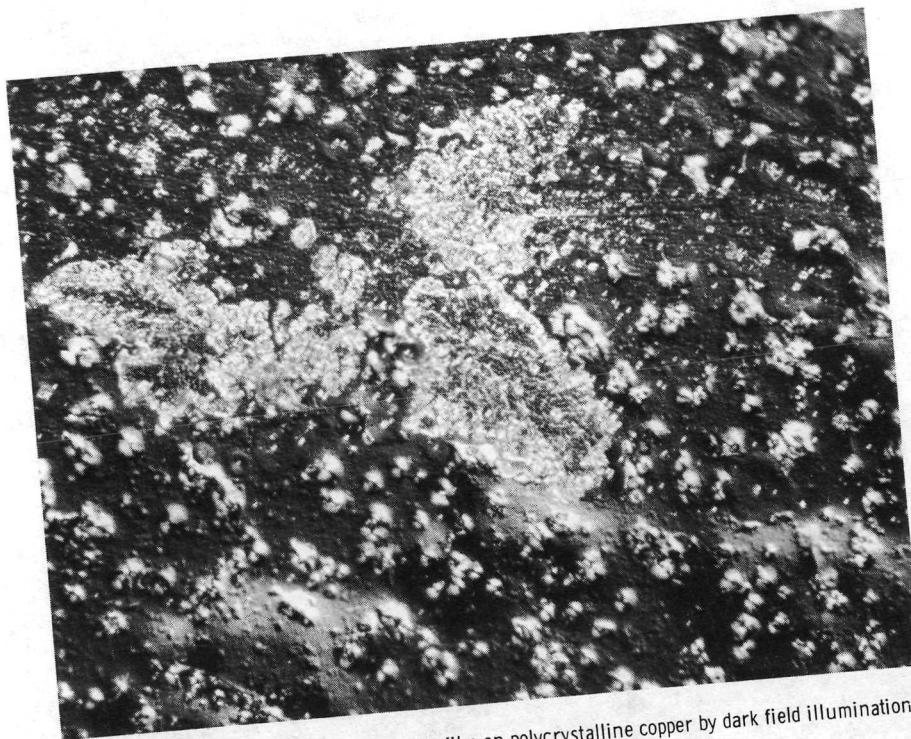


Figure 3. - Sputtered molybdenum disulfide film on polycrystalline copper by dark field illumination. X450.

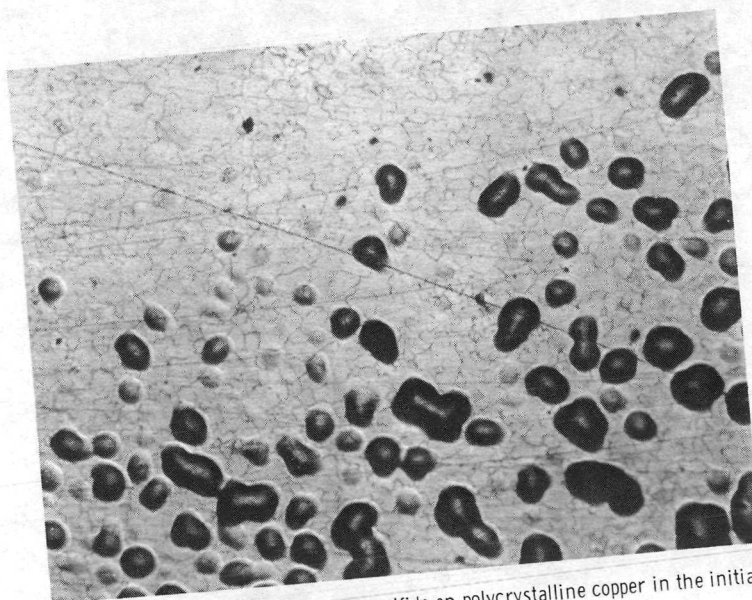


Figure 4. - Sputtered molybdenum disulfide on polycrystalline copper in the initial state of film formation. X80.

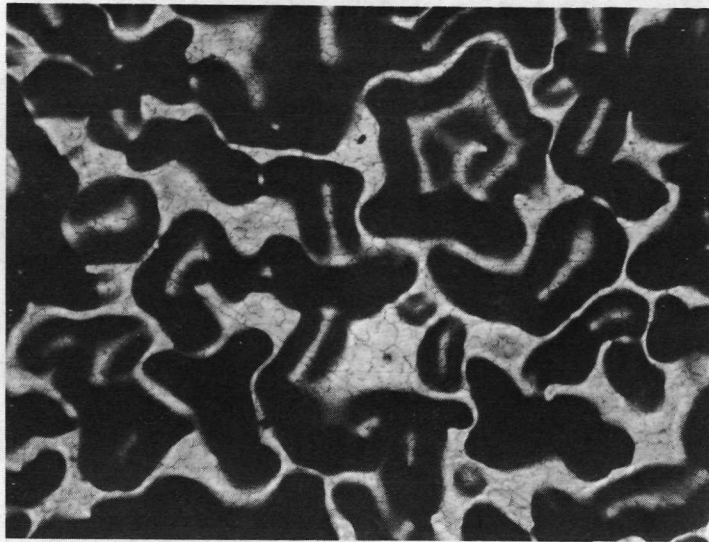


Figure 5. - Sputtered molybdenum disulfide on polycrystalline copper in the final state of film formation, with blistering. X80.

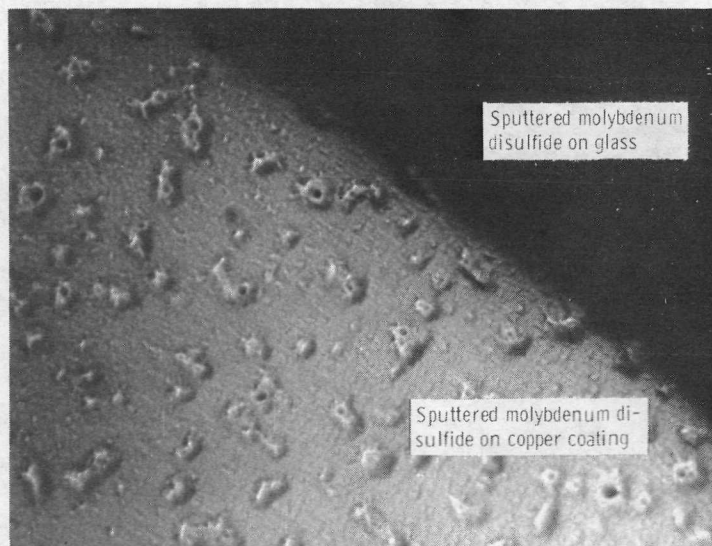


Figure 6. - Sputtered molybdenum disulfide film on glass and on glass precoated with evaporated copper. X150.

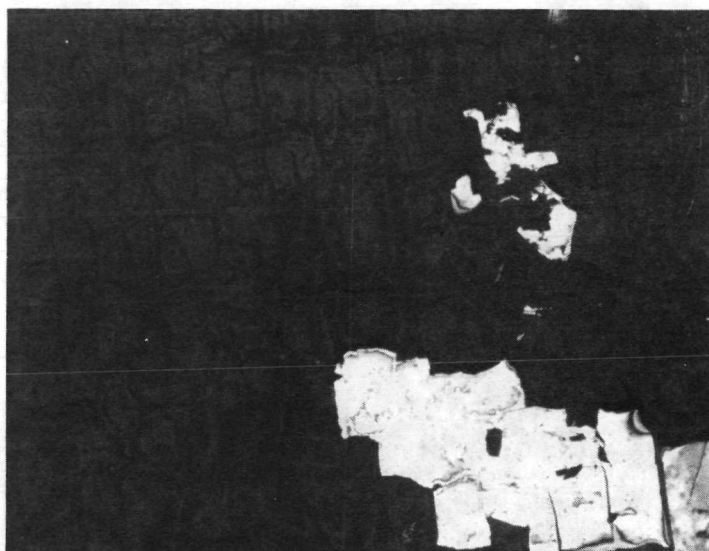


Figure 7. - 440C steel first ion plated with silver, then sputtered with molybdenum disulfide. X45.

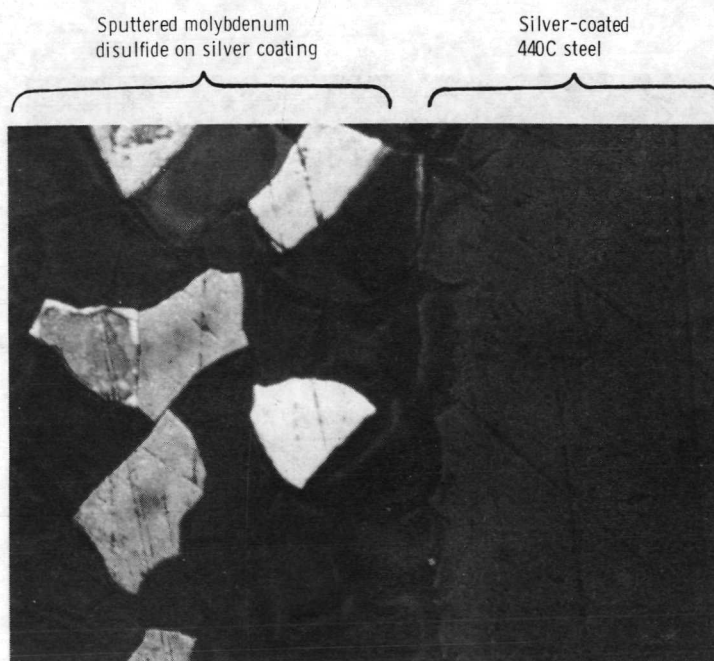


Figure 8. - 440C steel first ion plated with silver, then sputtered with molybdenum disulfide. X120.

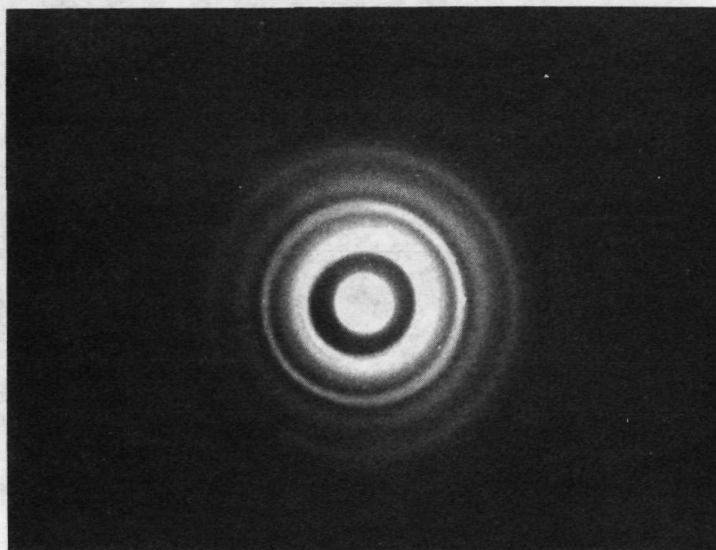


Figure 9. - Electron diffraction pattern of sputtered molybdenum disulfide film on copper.

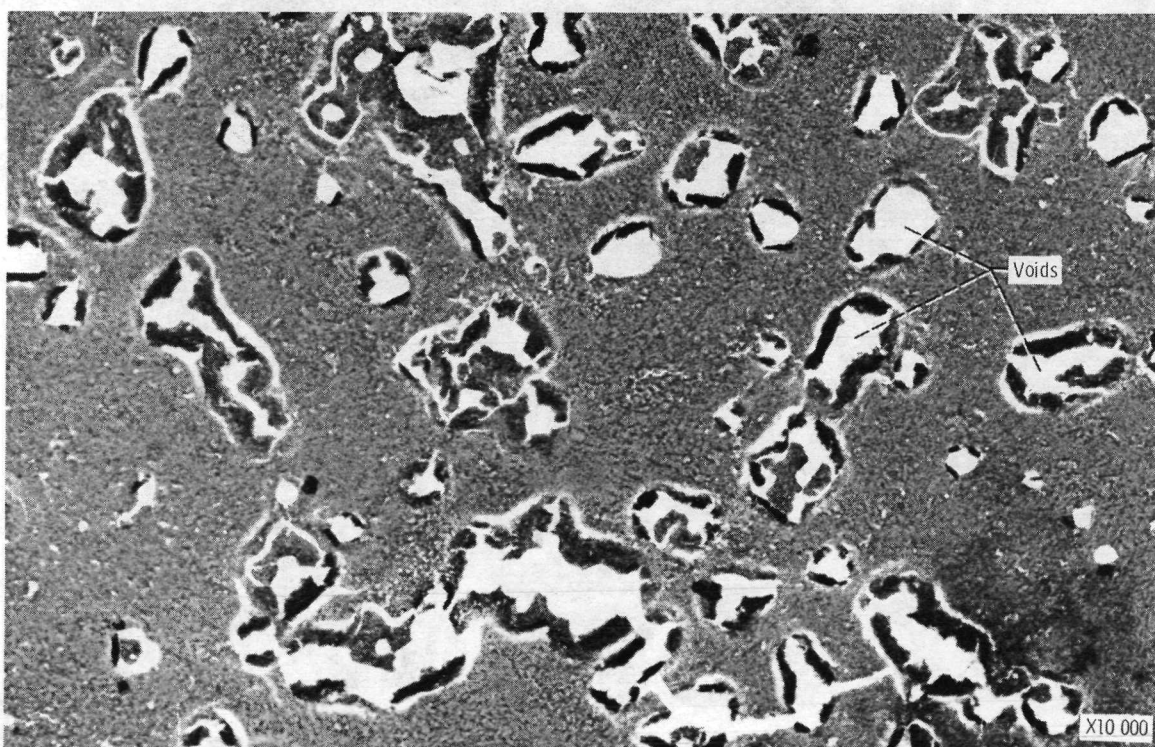
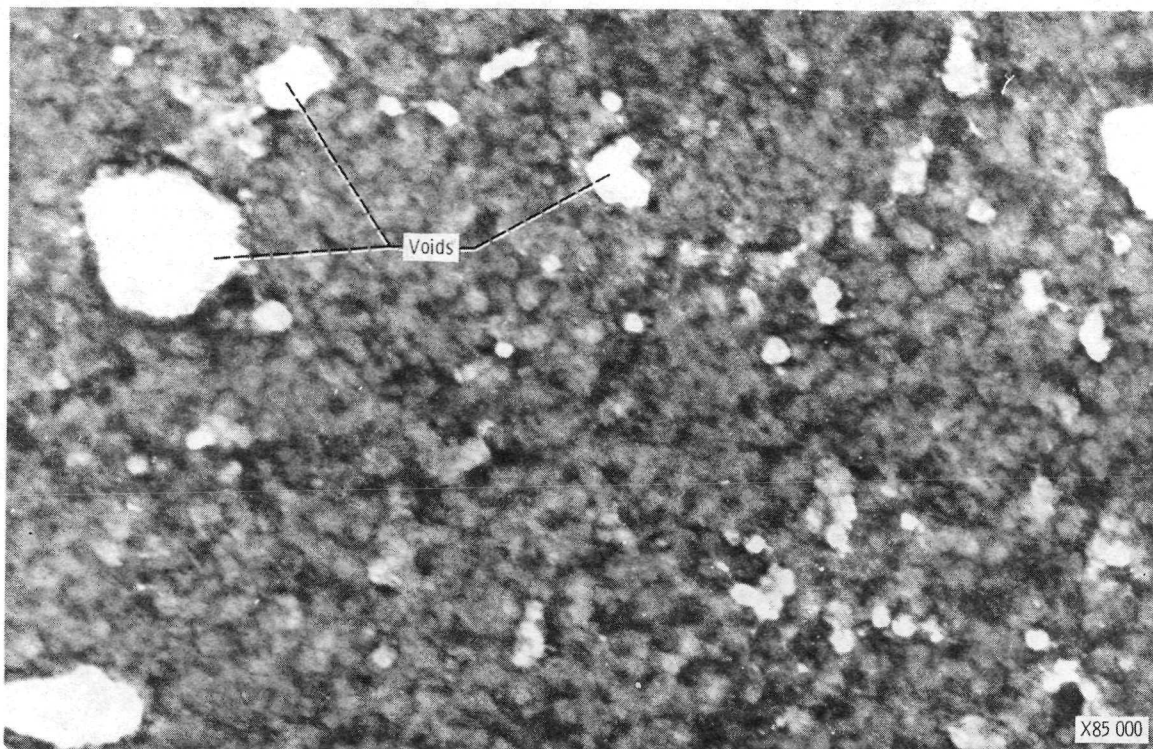


Figure 10. - Electron transmission micrographs of sputtered molybdenum disulfide on copper.

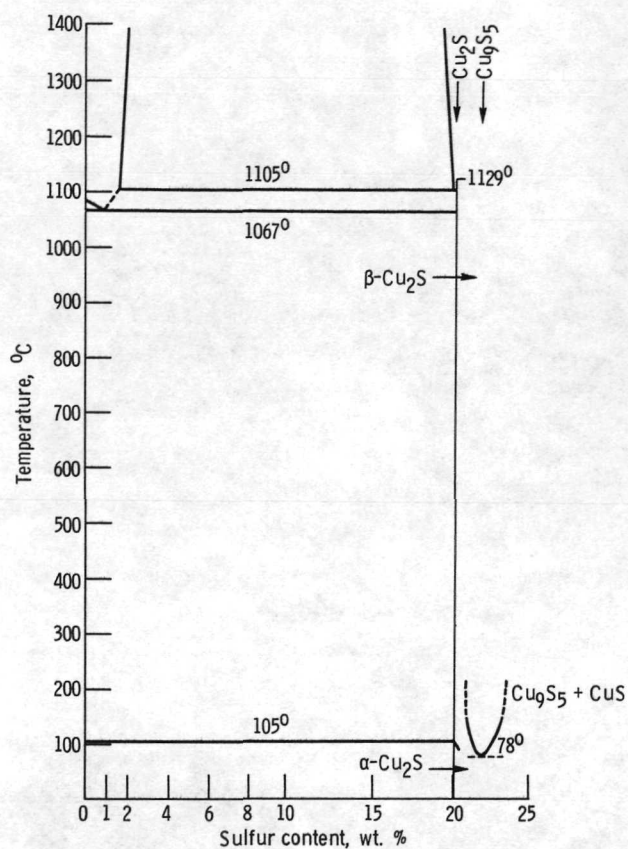


Figure 11. - Copper-sulfur phase diagram (from ref. 5).

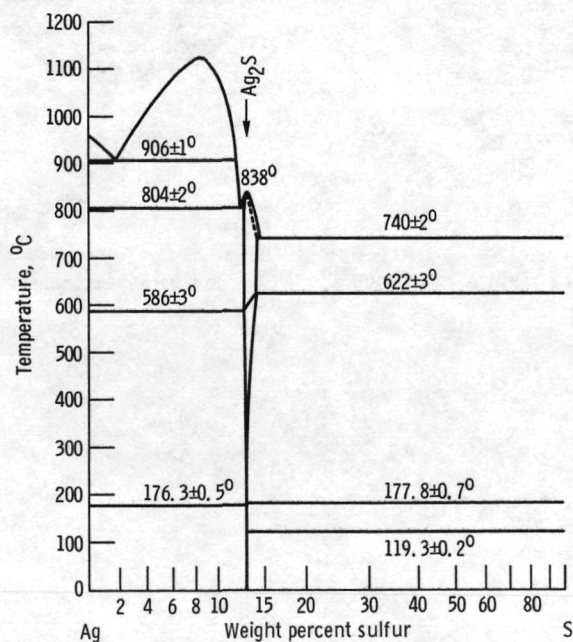
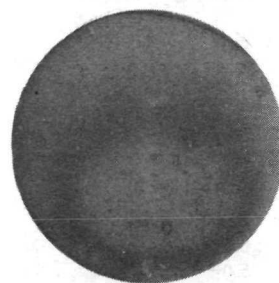


Figure 12. - Silver-sulfur phase diagram (from ref. 5).



Polished

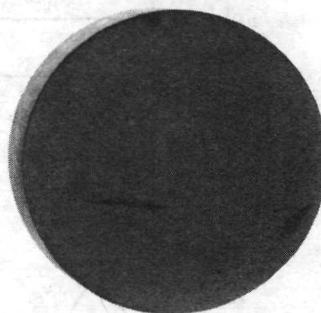
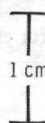


Oxidized

(a) Copper surfaces.



Polished



Oxidized

(b) Bronze surfaces.

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Figure 13. - Sputtered molybdenum disulfide film on copper and bronze surfaces.

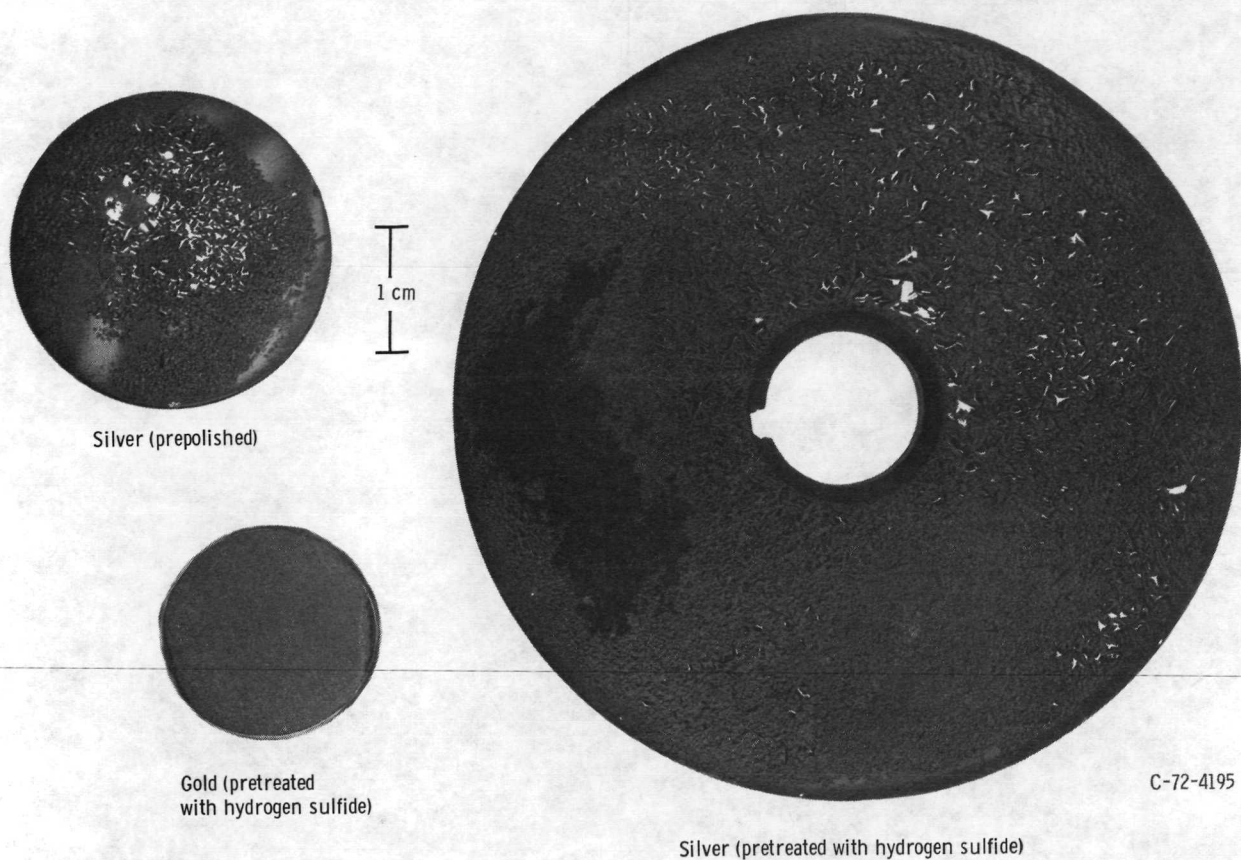


Figure 14. - Sputtered molybdenum disulfide film on prepolished silver, on silver pretreated with hydrogen sulfide, and on gold pretreated with hydrogen sulfide.



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